

# Leather Made To Fit Your Needs

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Leather is made by treating skins and hides so that they will not be acted upon by bacterial enzymes, will not be gelatinized by warm water, and will not become brittle when dried out. This treatment, known as tanning, gives them the desired softness, flexibility, and firmness.

Heavy leather is used where thickness, firmness, and solidity are needed, as in shoe soles, machine belting, and harness. For it, thick heavy hides from cows or other large animals are needed. Light leather is used where flexibility and softness are desired, as in shoe uppers, gloves, upholstery, garments, luggage, or chamois. It is usually made from the skins of small animals or young animals of larger species, such as goats, sheep, calves, or colts. It may also be made by splitting the hides of large animals into layers. Fur skins are a type of light leather in which the production of leather from the skin, while important, is secondary to the preservation and improvement of the fur.

Leather is of two general classes, heavy and light. Each requires its own type of tanning. The tanning of heavy leather used to take years; indeed, in many parts of the world today it still requires a whole year. Even in modern practice the tannage may last 2 to 3 months. Light leather is tanned quite rapidly; often only 2 days are required.

Leather is made in three stages. First, the hides or skins are prepared for tanning—the beamhouse operations,

so called because of the use of the beam, a convex sloping slab of wood upon which a hide or skin is placed while the operator removes hair or flesh with a knife. Second is the actual tanning operation. The third step is the finishing operation. Changes at any stage make a difference in the finished leathers. The best tanning process is the one in which the methods used in any step harmonize with those used in other steps to give the desired final effect.

TANNERS usually receive hides and skins dry or cured; that is, enough water has been removed, usually by salting, to prevent spoiling. Usually the hair is still on the hides and must be removed before tannage. As the wool on sheepskins is more valuable than the skins, it is generally removed by the grower or the wool puller, and the skins reach the tanner in a pickled condition—that is, preserved with a solution of sulfuric acid and salt.

The first step in the preparation of hides or skins for tanning is soaking in water to clean off accumulated dirt, to remove excess salt, and to restore some of the water lost in drying.

The second step is to soak them in a lime solution, usually containing sodium sulfide, to loosen the hair and epidermis, which are then removed, commonly by unhairing machines. The adhering connective tissue, or flesh, is then removed, and the hides or skins are scudded. Scudding means scraping by a blunt blade, which removes the remnants of the glands, hair roots, lime soaps, and dirt. Some of the lime is then removed by washing with water or with acids or deliming agents to remove more of it.

The tanner changes these operations to get the kind of leather he wants.

If he makes hard, firm sole leather,

he tries to prevent loss of hide substance and to get a firm, plumped hide. He soaks and limes for only a short time; he uses lime liquors which are sharp (alkaline) and not too mellow and which contain enough sodium sulfide for rapid unhairing. He delimes by merely washing some of the lime from the hides with water.

The tanner of soft, flexible, light leather soaks and limes for a long time. He gets a mild action by the use of a mellow lime liquor made by using the same liquor for several packs of skins. He can also get a mild action by using arsenic sulfide instead of sodium sulfide.

A tanner must be on the alert to change his methods according to the kind of hides or skins he gets. These come to him from many sources and may be hard as flint or soft and flexible. No matter in what condition he gets them, he must know what to do so that they will be as nearly alike as possible on leaving the beamhouse to be tanned.

After the beamhouse treatment, skins for soft, flexible leather need to be thoroughly delimed and made flat and flabby. The tanner does that by bating. Bates formerly consisted of suspensions of dog or bird dung; now they are commercial preparations, usually a mixture of pancreatic enzymes and ammonium chloride. The tanner may change the concentration, time, and temperature to suit his needs. Some skins after bating are pickled—treated with a solution of sulfuric acid and salt. The acid brings the skin to the necessary condition for tannage. The salt prevents the excessive swelling that would otherwise be caused by the acid. The effects of the pickling may be changed by concentration, temperature, and time of the process.

The hides or skins are now ready for tannage. If you look at an ordinary shoe you can see the difference between the two types of leather. The upper is a typical light leather and the sole is a typical heavy leather—or at least the tanner hopes so. Most sole leather is tanned with vegetable tanning extract

made from barks, woods, leaves, or pods of natural vegetable origin. Most upper leathers are chrome-tanned—that is, tanned with chromium mineral origin.

Heavy leather is usually tanned in solutions of vegetable tannins by a countercurrent system. The limed, unhaird, and partly delimed hides come into contact first with a weak, non-astringent (mellow) liquor, which has already been used for the tannage of more thoroughly tanned hides. After a day, the liquor is replaced by one of slightly higher tannin content and greater astringency. The process is repeated for several weeks, each liquor being stronger and more astringent than the preceding one. The liquor from the final tannage goes on less tanned leather and so on until finally, when it has become weak and mellow, it is used for the first tannage. Thus the leather and the liquor proceed in opposite directions through the tanyard. This countercurrent system is necessary because if hides were put into strong liquors they would be case-hardened—tanned hard on the outside and left raw inside.

The system allows an almost infinite variation to produce different types of leather—the tanner can make his leather more firm or more flexible or lighter or darker by his choice of tanning materials. He can shorten the time of process or lower the cost by the proper blend of different materials.

Tanners formerly made their liquors directly from the bark. Now most of them use a strong liquid extract, or a solid or powdered extract, made by a manufacturer of tanning materials.

In the early days, tanning methods were based on the use of oak bark and later hemlock bark. But when oak and hemlock became scarce, tanners had to change their methods to fit new materials. The most widely used tanning extract is quebracho, from southern South America. A blend of quebracho extract with chestnut extract, our most widely used domestic material, forms the basis of most American tannages.

Quebracho extract, used in the usual sulfited form, penetrates rapidly into hide to give a leather that has good color and feel but tends to be flat and poorly filled. Chestnut extract gives a firm, well-filled leather, but it penetrates slowly if it is used alone and tends to make the leather too firm and brittle. The tanner blends the materials to modify the firmness or flexibility of the leather as he desires.

Tanning blends usually also contain other kinds of tanning extracts, which aid in acid formation, increase penetration, improve the color and general appearance, or lower cost. Myrobalans extract, made from the unripe nuts of the myrobalans tree of India, for example, is used to produce acid. Wattle extract, from the bark of the mimosa tree, now grown in South Africa, may be used to replace some of the chestnut or quebracho extract when high prices make that desirable. Sumac, most of which is now imported from Sicily but which grows wild in this country, is used to improve the color and feel of the leather. In all, several hundred different materials—woods, barks, pods, leaves, and roots—contain enough tannin to justify their use in tanning. But not very many of them are available to tanners in extract form, although enough have always been available to give wide selection.

Sometimes used in tanning blends is the so-called sulfite-cellulose extract, which is a solubilized lignin byproduct of the sulfite paper industry. Its tanning value is doubtful, but it lowers costs and probably has some value in modifying the character of the blend. There are also available a number of syntans. These are usually made from phenols and aldehydes in the same way as bakelite or other synthetic resins, except that they have been made soluble in water by treatment with sulfuric acid or other reagents. They are not true synthetic tannins, but in some cases give results similar to those of natural tannins, for which they may be substituted if their somewhat higher cost will permit.

With that wide variety from which to choose, the tanner has been able to change his blend of tanning materials almost at will to produce the desired effect. However, the trees which provided these materials are getting scarce, and although steps are being taken to develop new tanning materials, either natural or synthetic, it is certain that in the future the tanner will not have the wide choice he has had in the past. Instead of changing his tanning blend to modify the leather, he must now treat the available tanning extracts before use, or modify the tanning process, so that one tanning material may give effects formerly produced by a different type of extract.

To modify the properties of the finished leather, the tanner may also change the tannin content of the liquors at various stages of tanning. These liquors, with an average tannin content of 0.5 percent in the weakest and 9 percent in the strongest, may be made either stronger or weaker. Another factor is the purity of the liquors—the ratio of tannin to total soluble matter. A low purity makes soft and spongy leather; a high purity is required for firm leathers. The acidity, measured either as total acid or as pH (active acidity), also modifies the character of the leather. The hides carry lime over into the tanyard and it must be neutralized and the hides brought to the slightly acid condition necessary for tanning. Generally, enough acid is formed by the fermentation of the sugars present in tanning materials, but sometimes it is necessary to add a weak organic acid, such as lactic or acetic acid. An acid condition of the liquors is required to plump the hides to the swollen condition that gives firmness and fullness to the finished leather. Too much acid, however, may cause an overswelling of the hide and produce tender leather; it may even cause case-hardening. The best acid conditions are probably between pH 3.5 in the stronger liquors and pH 4.5, or perhaps slightly higher, in the weaker liquors.

Mineral salts or inorganic material

are also in tanning liquors. If they are salts of the weak acids, they lower the acidity of the liquor and reduce its plumping power. Almost all other types of mineral matter, while not affecting the acidity, reduce the plumping power. In either case, flat, poorly filled leather is made. The mineral matter comes into the tan liquors from the lime brought in by the hides, from the mineral constituents of the tanning material, or from the water used. The countercurrent system already described gives the tanner an opportunity to regulate the amount of mineral matter accumulating in the liquor. A faster flow of the liquors through the tanyard reduces this amount, but it also retards the mellowing of the liquor and cuts down the amount of acids formed by fermentation. One factor must be balanced against the other to determine the proper procedure.

The tanner may also modify the tanning processes. At first the hides are suspended in weak liquor in vats in the so-called rocker section and given a slight rocking motion. The hides stay in the rocker section until the tannin has penetrated them. The customary way of finishing the tanning has been to place the hides flat in vats, laying one over the other, sometimes separated by a thin layer of bark. They remained in these lay-away vats, in which the liquors were strengthened one or more times, for several weeks or months, until they were thoroughly tanned. Tanners have found that by increasing the time in the rockers, using stronger liquors, the time in the lay-aways may be shortened, or these vats eliminated. This greatly shortens the time of tanning. Another way to shorten it is to tan in revolving drums with strong liquors toward the end of the tannage. Some tanners believe that shortening the time by these methods is accomplished at the expense of some of the firmness and fullness desired in the final leather.

The tanner can modify the character of the leather in the finishing opera-

tions. Leathers must be lubricated with oil or grease. For sole leather a mixture of animal or fish oil, such as cod, with mineral oil and sulfonated oil is commonly used. For harness leather a mixture of greases, such as tallow, and oils, is used. To give the leather greater grease-holding capacity it is not tanned so heavily as sole leather is. The leather may be rolled to make it hard and firm, staked to make it flat and flexible, and brushed to polish it. Sole leather may be bleached to give it a lighter color. Loading materials, such as epsom salts, glucose, and sulfite-cellulose extracts, may be added to make it retain its thickness and firmness in the finishing operation. Finally, the leather must be dried—an important step that takes careful watching. The tanner may modify any of these procedures to get the kind of leather he wishes.

The tanning of light leather is a short process as compared to heavy-leather tannage. It starts in the beamhouse, already described.

For some kinds of light leather the tanner uses vegetable tanning materials, syntans, or mixtures of them. The skins may be tanned somewhat as in the early stages of heavy-leather tannage or they may be tanned by tumbling in a drum with a solution of the tanning extract. Sometimes finely ground sumac leaves and water are added to the pickled skins in a tanning drum and the skins are tanned by the tannin leached from the leaves while tumbling.

Some tanners, especially tanners of glove leather, use an alum tannage. They tumble the skins in a drum containing a solution of aluminum sulfate, made alkaline with sodium carbonate and containing salt to prevent swelling. Toward the end of the process the liquor is neutralized with enough borax or sodium bicarbonate to precipitate the alum thoroughly in the skins. A mixture of egg yolk, oil, and flour is rubbed well into the leather, which is then allowed to dry and age for several weeks before being washed and fin-

ished. Alum tannage is also used for furs. In that case, the alkaline aluminum sulfate is generally made into a paste with flour and oil and rubbed into the flesh side of the skin.

Some tough, white leathers are tanned with formaldehyde. Formaldehyde, however, is used more as a pretannage than as a single tanning agent. It either imparts new characteristics to the finished leather or it aids in tannage with the other material. The skins are tanned with dilute solution of alkaline formaldehyde, which combines with the skin substance to form a type of leather. The alkalinity must be carefully regulated. The liquors will not tan unless sufficiently alkaline, but if they are too alkaline the leather will be brittle.

Chamois leather is oil-tanned. Although originally made from the skin of the chamois goat, it is now usually made from the inner layer of sheepskins. By alternately impregnating the skin with cod oil or some other suitable oil and drying, the oil combines with the skin to give chamois leather.

The chrome-tanning process is used for most light leathers, especially shoe uppers. Chromic oxide formed from sodium dichromate combines with the skin to form this type of leather. The skins may be impregnated with an acid sodium dichromate solution by tumbling in a revolving drum, and then with chromic oxide formed directly in the leather by tumbling in a sodium thiosulfate solution in a similar drum. In most cases, however, the sodium dichromate is reduced to chromic acid before being used and a tanning liquor is made from the acid. Bated skins from the beamhouse are pickled in acid and salt and drummed until tanned. They are then neutralized with a mild alkali, washed, and finished.

Several other methods for tanning light leather are used to a limited extent. There are so many ways of tanning light leather that it is probable that no two tanneries operate in exactly the same way. Every tanner has his own beamhouse procedures and his

own methods of preparing tanning liquors and adjusting the strength, acidity, and ratio of liquor to leather. He determines the time of tanning, the temperature, the mechanical methods, the degree and manner of neutralization, and the amount and type of neutral salts to give him the effect on the leather that he wants.

The finishing operations, particularly staking, have a greater effect on light leathers than on heavy leathers. Most leathers, left to dry by themselves, become hard and brittle because of adhesion of the fibers, but if they are flexed repeatedly at the proper stage of drying the fibers become separated and do not adhere when dry. When the Indians tanned deerskins for buckskin leathers, the squaws did the job by chewing on the leathers. Staking formerly was conducted by hand over a rounded blade fixed vertically. Sometimes the operator used his bare knee instead of the blade; the process is still largely used for glove leather but for other leathers has been replaced by machines.

Tanners may combine different kinds of tannage to make the kind of leather they want. For example, heavy leathers may be chrome-tanned and finished with a vegetable tannage. The time of tannage is thus shortened and the leather retains the properties of a vegetable tannage and acquires new properties, such as resistance to moist heat. Some light leathers are pretanned with formaldehyde before retannage with chrome, alum, or oil to give greater flexibility and resistance.

R. W. Frey and C. W. Beebe found that a combination chrome- and vegetable-tanned bookbinding leather has the resistance to acid deterioration of chrome leather combined with the workability and good appearance of vegetable-tanned leathers and that the vegetable-tanned leathers retanned with alum showed the same effect.

C. W. Beebe, J. S. Rogers, and W. F. Happich discovered that retanning vegetable-tanned insole leather with alum solution, suitably stabilized, im-

plifts resistance to moist heat and to deterioration by molds. In preliminary tests they found that the serviceability of such vegetable-tanned leather may be greatly increased by alum retannage.

Tanners now have the benefit of research results in changing their tanning processes to give them the leathers they wish. G. D. McLaughlin and E. R. Theis, in *The Chemistry of Leather Manufacture*, give the results of investigations which showed that sodium sulfhydrate, instead of sodium sulfide, or methylamine may be used as an unhairing agent in the beamhouse. New sources of tanning materials are being developed, but it is probable that the choice of such materials may be restricted. Therefore, it is of interest to investigate methods of modifying existing tanning materials. Sulfiting quebracho to increase its solubility and ease of penetration into the leather is now an accepted practice.

P. Chambard reported that during the war French tanners modified chestnut extract by increasing the solubility and pH to give it some of the properties of quebracho extract, which was almost unobtainable. In the development of canaigre extract, T. C. Cor-

don, C. W. Beebe, and J. S. Rogers have devised methods for fermentation of the sugars present to increase the purity of the extract. Tanners usually want high-purity extracts for the production of firm leathers.

Some of the new syntans (developed by H. G. Turley and J. H. Highberger, A. H. Bump and F. O'Flaherty, A. H. Winheim and E. E. Doherty) appear promising. Sulfonyl chloride has been proposed by M. F. White, W. T. Roddy, and O'Flaherty as a substitute for cod oil in making chamois leather. E. R. Theis and T. Kleppinger have found that stabilizing or "masking" salts have been found capable of improving chrome leather. Stabilizing salts of the same type have aided in the alum retannage of heavy vegetable-tanned leathers by increasing the penetration of the aluminum salts.

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